International Journal of Engineering Research (ISSN : 2319-6890)
Volume No.2, Issue No.2, pp : 172-177 01 April 2013

Preparation, Micro-hardness Characterization on Untreated and Treated with Electric Stressed Samples on the Inorganic Tunable Laser Dye Rhodamine Doped PMMA

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Abstract

Effect of Load, Load dependent nature of Micro hardness measurement and Doping Effect on untreated samples and Micro hardness studies on the effect of charge due to electrical stress on the samples of pure and Rhodamine doped PMMA with different weights proportions have been carried out using Vicker's micro hardness testing for hardened networks plasticization and crystallization. Some selected samples are used to study the electrical stress, with the help of thermostat controller at different polarizing temperatures and fields in thermally stimulated depolarization current due to dipole orientation or trapping of space charges, which gives the information about uniform polarization.

Keywords: Polymeric Material, Micro hardness, doping effect, Electrical stress

1. Introduction

Polymers are used extensively in many applications in thin film form; for example as free standing films, or as coatings which are next to rigid substrates. In electronic packaging, adherent epoxy under fills can be used to modify the localized stress concentrations [1], which can arise due to differences in coefficients of thermal expansion of the different materials. The mechanical state within the polymer necessarily varies from point to point within the thin film, as can the strength of the adhesion between the polymer and the substrate. In the past decade many advances have been made in the field of optical materials, that is tunable solid state lasers, non-linear sensors, luminescent solar concentrators and optical sensors. One of the most important inorganic dye useful as tunable laser material Rhodamine (Rh 6G) was introduced in the year 1967. PMMA is considered as one of the most efficient dye matrices with excellent optical, thermal, photochemical and dimensional stability [2]. As such it has been widely used for laser and non-linear optical materials. In the present work, effect of Load, Load dependent nature of Microhardness measurement and Doping Effect on untreated samples and Microhardness studies on the effect of charge due to electrical stress on the samples of pure and Rhodamine doped Polymethylmethacrylate were investigated.

2. Experimental Details

The experimental details regarding the preparation and microhardness studies of various pure and Rhodamine doped PMMA samples have been described in this section.

2.1 Preparation of Samples

Various pure and doped samples which are in the form of thick films of 60 to 90 µm thickness, having different ratio of Rhodamine (Rh6G) doped with PMMA films of different composition of PMMA**:** Rh (6G):**:** 2gm**:** 0.005mg, 2gm**:** 0.05mg, 2gm**:** 0.5mg and 2g Pure PMMA ratio were prepared by the solvent cast technique. In order to investigate the effect of electrical stress on the microhardness behavior some of the samples were subjected to step fields of 10 and 25 kV/cm at various temperatures 70 and 110 °C. For this, sample was sandwiched between two electrodes of the electrode assembly fitted inside an oven. The assembly was heated and the desired temperature was maintained, for 1/2 an hour. The step field was then applied and maintained for 45 minute at the desired temperature. The samples were then cooled down to the room temperature with the applied step field still on. The total time of application of electric field (which leads to polarization) was kept 1/2 hr. in each case. The samples so treated were then removed for microhardness measurements.

2.2 Measurement of Microhardness

Microhardness measurements on treated and untreated film samples (60-90 µm thickness) were carried out by means of mhp-160 microhardness tester. Indentation was made with a Vickers's diamond pyramidal indenter having a square base and pyramidal angle of 136° between the opposite faces attached to Carl Zeiss NU-2 microscope. Sample of dimension 0.25 cm^2 was cut and fixed, firmly with non reactive adhesive on an optically plane glass plate in such away that surface to be indented was perfectly horizontal. The plate along with the sample was then mounted on the stage of microscope, so as to avoid any displacement of

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samples during indentation. The load ranging from 10 to l00 g was applied softly at a steady rate. Care was taken to avoid any jerks and variation during indentation. The time of application of load was kept 30 s in each case. The length of the diagonal made by the indenter was measured by a micrometer eyepiece with an objective of sufficient magnification.

The mean value of diagonal was used for the calculation of hardness number. For each value of load, several indentations were made and average hardness number was computed. The samples containing different samples of Rhodamine (Rh6G) doped PMMA Films of different composition of PMMA**:** Rh (6G)**::** 2gm**:** 0.005mg, 2gm**:** 0.05mg, 2gm**:** 0.5mg and 2g Pure PMMA ratio were indented for microhardness measurement.

The following relation has been used to calculate the Vicker's hardness H_v:

$H_v = 1.854 \times L / d^2$ Kg/mm^2

Where L is the load in kg and d is the length of the diagonal of indentation, in mm.

3. Results and Discussion

The result of variation of microhardness with varying ratio of pure and Rhodamine doped PMMA with different load; composition and field variation are discussed below.

3.1 Microhardness of Untreated samples

(A) Effect of Load

Microhardness of a material plays a significant role on the chemical and morphological character of the material, and therefore, by a suitable choice of components of the material, the hardness of the material may be desirably altered. The effect of load on the microhardness of pure PMMA and 0.005mg, 0.05mg, 0.5 mg Rh(6G)doped with PMMA are shown in Figure 1

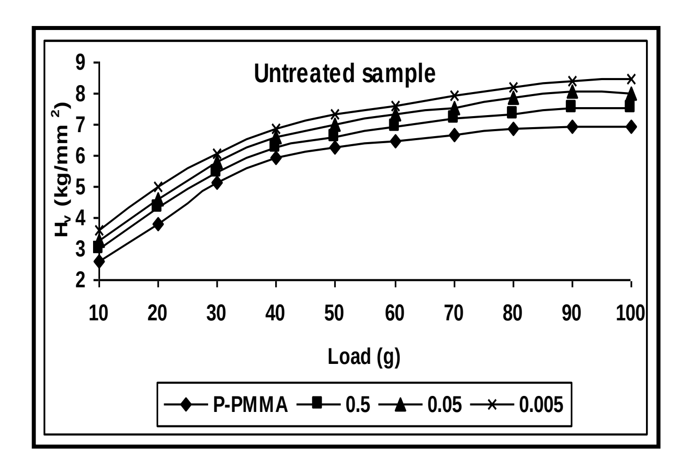


Figure 1 Variation of Hv with Load for untreated pure PMMA, 0.5 mg, 0.05 mg and 0.005 mg doped PMMA samples.

The value of Hv is minimum for pure PMMA and maximum for lowest doping of Rhodamine (Rh6G). The microhardness increases on decreasing the doping of Rhodamine (Rh6g) in PMMA. The result also shows that the value of H_v increases curvilinearly with increasing load (10-100 g) for different samples. The increase in H_v with load is due to strain hardening in the specimen. It is also noticed that the rate of strain hardening is greater at lower loads. The H_v attains a limiting value beyond the load at 60g for pure PMMA, 70g for 0.5mg, 0.05mg and 80g for 0.005 mg Rh (6G) doped PMMA.. The different values of the microhardness at saturation for pure PMMA, 0.005mg, 0.05mg, and 0.5 mg Rh (6G) doped with PMMA indicate the changes in the macromolecular structure and morphology due to which the related values of microhardness exhibit the hardening or softening characteristic of the material. Based on strain hardening phenomena [3] in the polymers, there is a spectrum of micro mode of deformation in polymer chain. Each micro mode is activated by characteristic temperature and strain conditions. When sufficient number of micro modes becomes active, large- scale plastic deformation begins.

According to Amontons and Chery [4] phenomena, the microhardness may be correlated with frictional force. The coefficient of friction decreases with increasing load and the frictional force is found to increase linearly with increasing load. Hence, the variation of H_v with load is curvilinear. On applying load, the polymer is subjected to some strain hardening. When H_v value tends to become constant, the polymer is completely strain hardened. The rate of strain hardening in various samples is related to weight percent ratio of polymers in the blend, which governs the degree of cross-linking in the blend. Hence, the different saturation load values are observed for different samples. The saturation value of H_v beyond 60g may be due to permanent deformation caused by chain-chain slipping in polymer system.

(B) Load dependent nature of Microhardness measurement:

The load dependent nature of microhardness of materials can be determined by strain hardening index of Meyer's law. This gives the relation between load L and length of diagonal d:

$$L = a.\ d^{n}$$

Taking logarithm both sides of the equation, we have

$$\log L = \log a + n \log d$$

Where, 'a' is constant i.e. load for unit dimension and 'n' is the logarithmic index number, which is the measure of strain hardening.

The plots of log L versus log d for 0.005mg, 0.05mg, and 0.5 mg (Rh 6G) doped with PMMA and pure PMMA are

shown in **Figure 2(a)** to **2(d)**. All the plots show two straight lines with different slopes for low load and high load regions. The value for n for 0.005mg, 0.05mg, 0.5 mg (Rh 6G) doped with PMMA and pure PMMA are listed in **Table (1)**. It is evident from Meyer's law that H_v increases continuously with load (in low load region) when n > 2. The value of n approaches around 2 in the saturation load region at which Hv becomes independent of load. Thus, in the low load region where Hv increases with load, the value of n is greater 2. Hence, the logarithmic index number n can be used as a measure of strain hardening.

Table (1): The value of 'n' for 0.005mg, 0.05mg, 0.5mg Rhodamine (Rh6g) doped PMMA and pure PMMA

Sl.No.	Sample PMMA: Rh(6g)	Slop in low load region	Slop in high load region
1	2g: 0.005mg	2.04	2.22
2.	2g: 0.05mg	2.08	2.23
3.	2g:0.5mg	2.09	2.20
4.	Pure PMMA	2.11	2.21

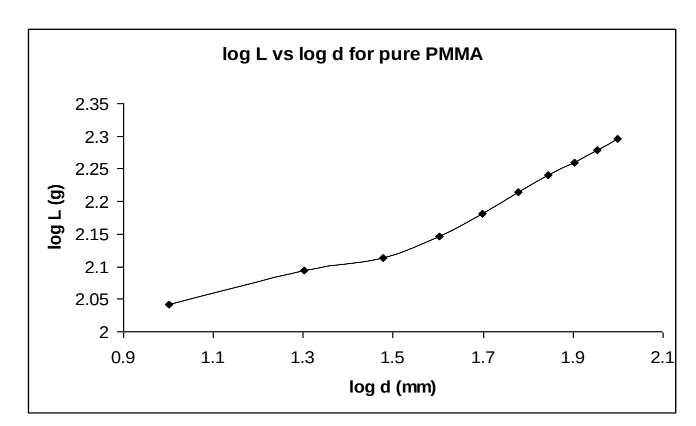


Figure 2 (a) Variation of load (log L) with diagonal (log d) for pure PMMA

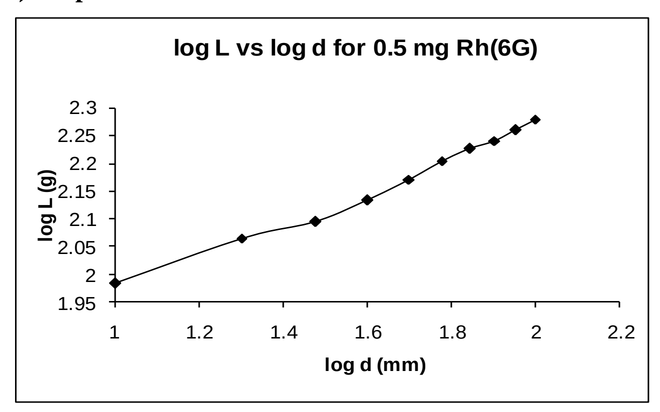


Figure 2 (b) Variation of load (log L) with diagonal (log d) for 0.5 mg Rh(6G) doped PMMA

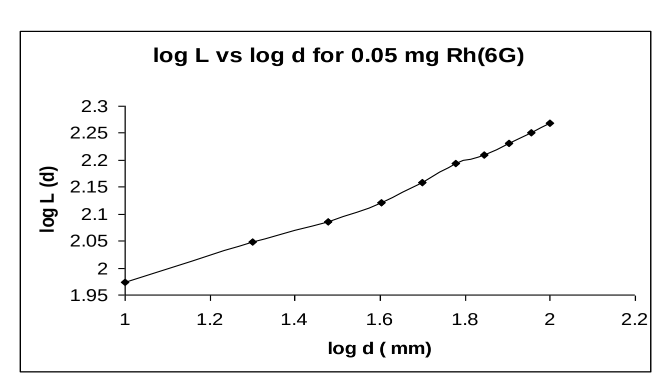


Figure 2 (c) Variation of load (log L) with diagonal (log d) for 0.05 mg Rh (6G) doped PMMA

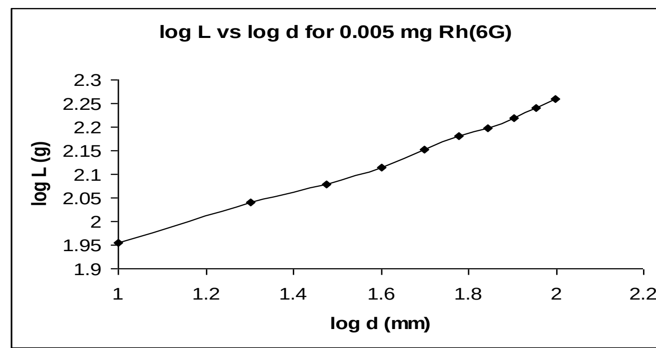


Figure 2(d) Variation of load (log L) with diagonal (log d) for 0.005 mg Rh (6G) doped PMMA

According to the theory of Pasco and Taber [5] indicates the condition 2 < n > 3; for explaining the nature of elastic and plastic contacts. According to observation made out of H_v-load studies, the different values of n in different load regions reflect the elastic –plastic characteristic of deformation.

(C) Doping Effect

In **Figure 3** variation of H_v with varying ratios of Rhodamine (Rh6G) untreated 0.0mg (pure PMMA), 0.5 mg, and 0.05 mg, 0.005 mg doped with PMMA at various loads ranging from 20 to 100g.

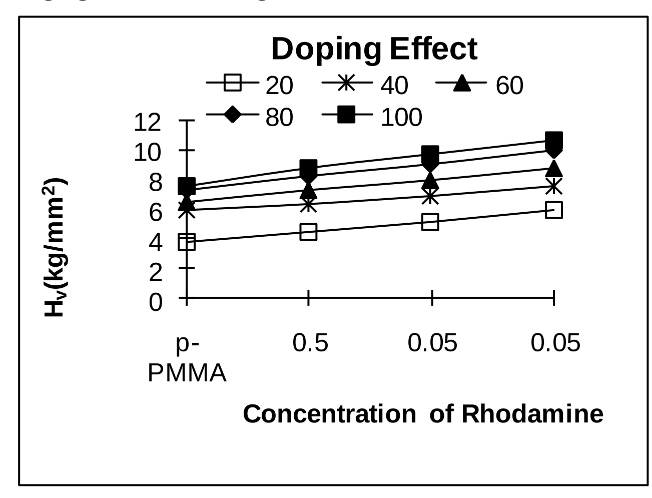


Figure 3 Variation of Hv with varying ratios of untreated pure PMMA, 0.5 mg, 0.05 mg, 0.005 mg Rhodamine (Rh6G) doped PMMA at different loads

Initially, it is evident that the value of H_v is increasing gradually with decreasing the doping of Rhodamine in PMMA at low and high load region. The value of H_v is highest and optimum value is obtained for samples with lowest doping concentration (0.005 mg) of Rhodamine in PMMA. This shows that the doped Polymethylmethacrylate samples in relatively low weight proportion, 0.005 mg Rh (6G), the hardening is maximum as a result of maximum crosslink density developed with the interfacing of molecules of Rhodamine in PMMA chains to produce network structure [6]. However, the density of this crosslinking decreases with increase in the doping concentration of Rhodamine beyond 0.005 mg as the level of microhardness of these specimens' decreases. Moreover, the microhardness of all doped specimens are still higher than that of pure PMMA specimen, which is an indicative of over all hardening effect as a consequence of doping of PMMA with Rhodamine. Thus the crystalline nature of Rhodamine doped PMMA imparts increase in the microhardness.

3.2 Microhardness of samples treated with electric field

In order to investigate the effect of thermal and electrical aging on the microhardness behaviour of pure and Rhodamine doped Polymethylmethacrylate samples with various ratios the samples were prepared and electrically stressed [7] by applying a fixed step voltage of 400 volts at a fixed temperature of 60^oC. For this, specimens of 100 microns thickness were sand witched between the two metal electrodes of the measuring cell, which was mounted inside the oven and heated to a desired temperature. After half an hour, the desired step voltage was applied for a time period of 45 minutes while the temperature was maintained at the desired fixed value 60^oC. The specimen was then slowly cooled to room temperature within 45 minutes, while the electrical field was still on. The total time of application of electric field was kept 1 ½ hour in each case. The electric field was then removed and the thermally and electrically aged specimen was taken out for microhardness measurements.

Figures 4 and **5** reveal the variation of Hv with load for electrically stressed specimen of pure PMMA, 0.5 mg, 0.05 mg, 0.005mg Rhodamine (Rh6G) doped PMMA at 70^o C and field 10 kV /cm. and 110^o C and field 25 kV / cm.

It is evident that the value of microhardness H_v, is increased in comparison to untreated samples and saturation point of untreated samples are obtained in low load region while for electrically stressed samples the saturation points are obtained in high load region, which shows that the train hardening effect is more in comparison to untreated samples. The value of H_v is gradually increasing from lower load to higher load region for both untreated and electrically stressed samples, which exhibits the crosslinking network [8] also formulated as applied load is increasing. The value of Hv is lowest for pure PMMA and highest for lowest doping of Rhodamine in PMMA, which explains the doped molecules is more hardened than pure samples with better crosslinking between the dye material and the polymer chains of PMMA. It is also clear that the crosslinking of Rhodamine in PMMA is increasing with decreasing the concentration of Rhodamine doped samples.

Furthermore, **Figure (4)** and **(5)** reveals the variation of Hv with load for electrically stressed specimen of pure PMMA, 0.5 mg, 0.05 mg, 0.005mg Rhodamine (Rh6G) doped PMMA at polarizing temperature of 70^o C and polarizing field of 10 kV /cm. and polarizing temperature of 110^o C and polarizing field 25 kV / cm. It is clear that the value of H_v increases in comparison to the untreated (non-electrically stressed) specimens at both the field strength. However, the level of increase in microhardness approximately remains unaltered with increase in field strength from 10 kV/cm to 25 kV/cm. The application of electrical stress causes bulk charging and these charges are trapped and frozen in. The trapped charges cause hindrance to the polymer chain mobility and thus causing stiffness to the otherwise flexible chain, which ultimately leads to hardening of specimens.

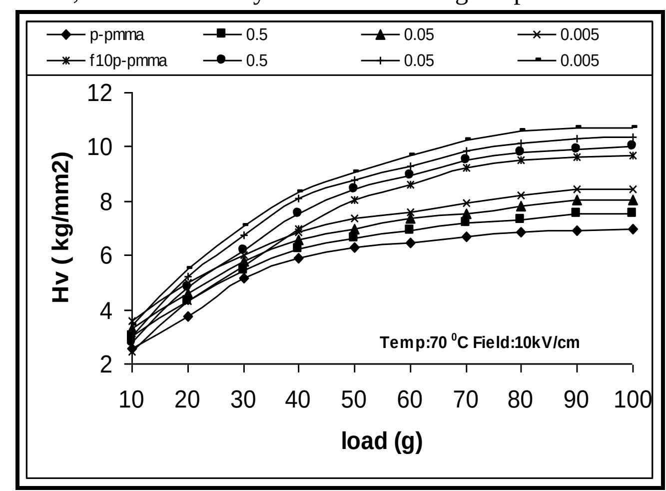


Figure 4 Variation of Hv with load for untreated and electrically stressed specimen of pure PMMA, 0.5 mg, 0.05 mg, 0.005 mg Rhodamine (Rh6G) doped PMMA at 70^0 C and Field 10 kV /cm

It is well known that polymers have flexible chains and internal rotation of parts chain is possible thermally [9-10]. Owing to thermal motion the spatial arrangement of atoms, keep continuously changing leading to different conformations. Each confirmation corresponds to a definite value of potential energy of the molecule, which is determined by all the interactions between atoms, electrons, nuclei etc.

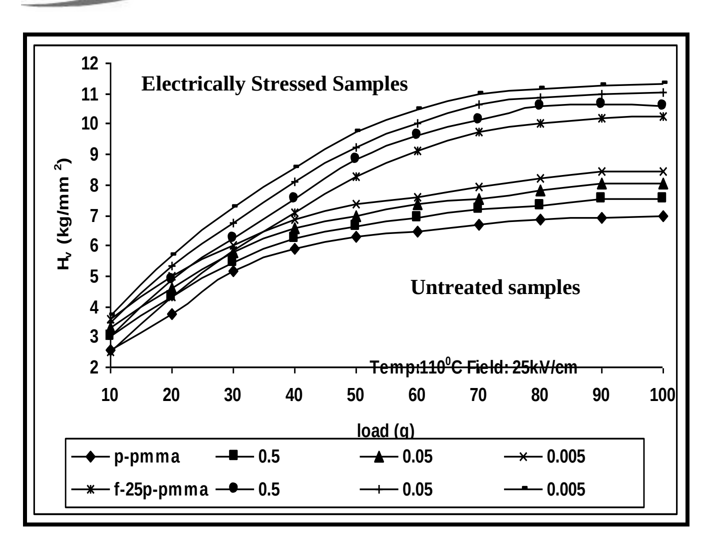


Figure 5 Variation of Hv with load for untreated and electrically stressed specimen of pure PMMA, 0.5mg, 0.05mg, 0.005 Rhodamine (Rh6G) doped PMMA at 110 ^{0} C and Field 25 kV /cm

The energy required by the molecule to move from the position with minimum potential energy to maximum potential energy is called hindrance potential or rotational barrier. If supply of kinetics energy is small, the groups of molecules do not rotate but only vibrate about the position of minimum potential energy executing restricted or retarded internal rotation. Bresler and Frenkel [11] showed that internal rotation is retarded by interaction between atoms not bonded chemically to each other. There may be interaction between atoms of the same chains (intermolecular) or between atoms belonging to units of neighboring ionic interactions, orientational interactions, deformational interactions and dispersional interactions. Besides intramolecular hydrogen, interactions are also possible. Under the influence of an external force field, chain exhibits kinetic flexibility, which refers to rate of transition from one position of energy to another, chain can uncoil to a certain extent depending on the relation between the field energy and potential energy barrier. The rate of conformational transformation depends on the ratio of potential energy barrier and the energy of external influence [12]. Thus, rotation of units and their passage from one position of potential energy minimum to another can occur only when there is ample supply of energy. Further, polymer links can assume only those positions in space, which are allowed by the presence of an interaction.

Thus owing to intermolecular interactions a real polymer chain assumes a smaller number of conformations than a freely joined chain. With insufficient supply of energy its units do not rotate but exhibit only torsional vibrations [13]. Polymers with intense torsional vibrations are flexible chain polymers while polymers with hindered rotation of chain parts are called rigid chain polymers. Prior to the application of the electrical stress field, the samples were kept at a high temperature and maintained for half an hour facilitating thermal movements of chains. Subsequent application of the electrical stress at this elevated temperature and hence the directing action of the polymer and this state is frozen in on cooling. It appears that in electrically stressed polarized samples. Inter and intra molecular interactions are minified in such a way that steric hindrance of rotation of chain or potential rotational barrier is increased, restricting kinetic flexibility of polymer chain. This yields a material, which is hard as compared to the untreated sample and hence the increase in the value of Hv is observed for electrically stressed[14] samples in the present case.

4. Conclusion

The different values of the microhardness at saturation for pure PMMA and Rh (6G) doped with PMMA indicate the changes in the macromolecular structure and morphology due to which the related values of microhardness exhibit the hardening or softening characteristic of the material. Based on strain hardening phenomena in the polymers, there is a spectrum of micro mode of deformation in polymer chain. According to observation made out of H_v-load studies, the different values of n in different load regions reflect the elastic –plastic characteristic of deformation. Moreover, the microhardness of all doped specimens are still higher than that of pure PMMA specimen, which is an indicative of over all hardening effect as a consequence of doping of PMMA with Rhodamine. It is evident that the value of microhardness $H_{v,}$ is increased in comparison to untreated samples and saturation point of untreated samples are obtained in low load region while for electrically stressed samples the saturation points are obtained in high load region, which shows that the train hardening effect is more in comparison to untreated samples. The cross linking density between the dye molecules with PMMA chains is found to be enhanced when they are kept under electrical stress at different polarization field strength and temperature, which yields in the increase in hardness related to untreated specimens. The degree of hardening increases both with the increase in the load and applied electric field strength. Thus, the Rhodamine doped PMMA samples can be developed with optimum weight proportions as a material having excellent mechanical strength.

Acknowledgement

The authors wish to acknowledge University Grants Commission – Central Regional Office Bhopal for financial assistance under Minor Research Project.

References

1. B. W. Mott, Micro indentation hardness testing, ButterWorth’s Scientific Pub. London, (1956) p.221
2. D. Tabor, Proc. Roy. Soc. 192(1948) 247

3. E. Bare, R. E. Maier, R. N. Teterson, SPE Journal 17(1961)1202
4. R. Bajpai, S. C. Datt, Indian J. Pure and Appl. Phys. 24(1986)254-255
5. S. K. Awasthi , R. Bajpai, Indian J. Pure and Appl. Phys. 26 (2001) 356-358
6. F. Macdonald, J. Phys. D. Appl. Phys. 9(1976)325
7. R. Bajpai, J. M. Keller & S. C. Dutt, Proc. Symp. IIT Kanpur (1987) 85-89
8. M. H. Ansari , R. Bajpai, S. C. Datt, J.Mater. Sci. 13 (1986) 3-8
9. D. Laborizza, J. Macromol. Chem. Macromol. 21(1988) 465-474
10. M. K. Kumar, R. Bajpai, S. C. Dutt, Polymer Testing 12 (1993) 31-34.
11. V. Dubey, P. Parasher, R. Bajpai, S. C. Dutt, Polymer Testing 11 (1992) 225-231
12. L. Boor, Proc. Amer. Soc. Test. Mat. 44(1944) 469
13. A. Tager, Physical chem. of Polymers Mir Pub. Moscow (1978) p 186, 234, 235,259
14. B. Merlin, J. C. Merino, J. M. Pastor & J. A. Desuja, Ferroelectrics 55(1981) 71